

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :

C11D 3/39, 3/395, 3/26

A2

(11) International Publication Number:

WO 98/07825

(43) International Publication Date:

26 February 1998 (26.02.98)

(21) International Application Number:

PCT/EP97/04097

(22) International Filing Date:

29 July 1997 (29.07.97)

(30) Priority Data:

60/024,479

23 August 1996 (23.08.96)

US

(71) Applicant (for all designated States except AU BB CA GB GH IE KE LK LS MN MW NZ SD SG SZ TT UG): UNILEVER N.V. (NL/NL); Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant (for AU BB CA GB GH IE KE LK LS MN MW NZ SD SG SZ TT UG only): UNILEVER PLC (GB/GB); Unilever House, Blackfriars, London EC4P 4BQ (GB).

(72) Inventor: MOSCHNER, Karl, F.; 169 Second Street, Troy County of Rensselaer, NY (US).

(74) Agent: UNILEVER N.V.; Patent Division, P.O. Box 137, NL-3130 AC Vlaardingen (NL).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published

Without international search report and to be republished upon receipt of that report.

(54) Title: N-ACYLIMINES AS BLEACH CATALYSTS

(57) Abstract

Novel bleaches, a method for bleaching substrates using these materials and detergent compositions containing same are reported. The bleaches are N-acylimines. Substrates such as fabrics may be bleached in an aqueous solution containing the N-acylimines and a peroxygen compound.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakistan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

N-ACYLIMINES AS BLEACH CATALYSTS

Field of the invention

The invention relates to bleach catalysts, compositions
5 containing same and a method for using the catalysts for
cleaning substrates, especially fabrics.

Background of the invention an the Related Art

Many household and personal care products are formulated
10 with an active oxygen-releasing material to effect removal
of stain and soil. Oxygen-releasing materials have an
important limitation; their activity is extremely
temperature dependent. Temperatures in excess of 60°C are
normally required to achieve any bleach effectiveness in an
15 aqueous wash system. Especially for cleaning fabrics, high
temperature operation is both economically and practically
disadvantageous.

The art has partially solved the aforementioned problem
20 through the use of activators. These activators, also known
as bleach precursors, often appear in the form of
carboxylic acid esters. In an aqueous liquor, anions of
hydrogen peroxide react with the ester to generate the
corresponding peroxyacid which oxidizes the stained
25 substrate. Commercial application of this technology is
found in certain fabric bleaching detergent powders
incorporating sodium nonanoyloxybenzene sulfonate. This
activator is typical of a class that features a phenol
sulfonate leaving group; see US-A-4,412,934.
30

While carboxylic acid ester activators and the like are
often effective, they are not catalytic. Once the ester has
been perhydrolyzed it can no longer be recycled.

35 Therefore, relatively large amounts of activator are
necessary. Amounts as high as 8% may be necessary in a

detergent formulation for bleaching fabrics. Cost for these relatively expensive activators is of major concern at such levels.

5 A significant advance in catalysis was reported utilizing sulfonimines in US-A-5,041,232, US-A-5,047,163 and US-A-5,045,223. Only a few of the reported compounds have been studied in any detail. More investigation needs to be conducted to identify catalysts of even greater activity.

10

Accordingly, it is an object of the present invention to provide novel bleach catalysts that can operate over a wide temperature range including that of under 60°C.

15 It is another object of the present invention to provide bleach catalysts which are effective at relatively low concentrations thereby achieving a cost effective stain removal system.

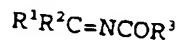
20 A further object of the present invention is to provide a method for bleaching stained substrates such as clothes, household hard surfaces including sinks, toilets and the like, and even dentures.

25 Other objects of the present invention will become apparent through the following summary, detailed discussion and examples.

SUMMARY OF THE INVENTION

30 A bleaching composition is provided including:

- (i) from 1 to 60% by weight of a peroxygen compound;
- (ii) from 0.01 to 10% of an oxygen transfer agent whose structure is:



35

wherein:

R¹ may be hydrogen or a C₁-C₄₀ substituted or unsubstituted radical selected from the group

consisting of phenyl, aryl, acyl, heterocyclic ring, alkyl and cycloalkyl radicals;

5 R^2 may be hydrogen or a C_1 - C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, $R^1C=NCOR^3$, nitro, halo, cyano, alkoxy, keto, carboxylic and carboalkoxy radicals;

10 R^3 may be a C_1 - C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, nitro, halo and cyano radicals;

15 R^1 with R^2 and R^2 with R^3 may respectively together independently form a cycloalkyl, heterocyclic, and aromatic ring system; and

(iii) from about 0.5 to 50% of a surfactant.

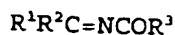
20 Additionally, there is provided a method for bleaching a stained substrate comprising the step of applying to the stained substrate an aqueous solution comprising a peroxygen compound and an oxygen transfer agent whose
25 structure is $R^1R^2C=NCOR^3$, with radical groups as defined above, the mole ratio of peroxygen compound to oxygen transfer agent being from about 250:1 to about 1:2.

Certain novel compounds are also provided whose structure
30 is $R^1R^2C=NCOR^3$ having radical groups as defined above, with the proviso that at least one of R^1 , R^2 , R^3 is substituted with a water-solubilizing functional group. Typical water-solubilizing groups include carboxylic acid, phosphoric acid, phosphonic acid, sulfuric acid, sulfonic acid, and,
35 especially, their salt derivatives and quaternary ammonium salts.

Detailed description of the invention

It has been found that N-acylimines operate even more effectively than sulfonimines as catalysts for activating peroxygen compounds to transfer active oxygen to stains.

- 5 Consumer and industrial articles can effectively be bleached to remove stains present on such articles. N-acylimines covered by the present invention are those whose structure is:



- 10 wherein:

R^1 may be hydrogen or a C_1 - C_{40} substituted or unsubstituted radical selected from the group the group consisting of phenyl, aryl, acyl, heterocyclic ring, alkyl and cycloalkyl radicals;

15

R^2 may be hydrogen or a C_1 - C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, $R^1C=NCOR^3$ nitro, halo, cyano, alkoxy, keto, carboxylic and carboalkoxy radicals;

20

R^3 may be a C_1 - C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, nitro, halo and cyano radicals; and

25

R^1 with R^2 and R^2 with R^3 may respectively together independently form a cycloalkyl, heterocyclic or aromatic ring system.

30

Often advantageous are N-acylimines having at least one of R^1 , R^2 , R^3 substituted with a water-solubilizing functional group. These functional groups may be selected from carboxylates, phosphates, phosphonates, sulfates, sulfonates in acid and salt form and quaternary ammonium salts. Suitable salts include those whose counterions are selected from alkali metal, ammonium, and C_2 - C_6

35

alkanolammonium cations.

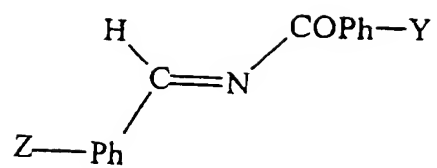
Amine functional groups may also be incorporated into R^1 , R^2 or R^3 to provide water-solubilization of the N-acylimines.
5 An example combining the amine and heterocyclic structure is that of pyridine.

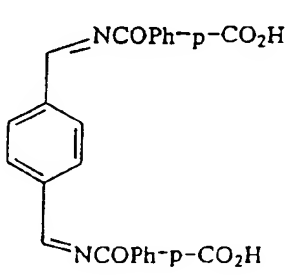
A water-solubilizing functional group is one which renders the N-acylimines soluble to the extent of at least 2 mg/l, preferably at least 25 mg/l, optimally at least 250 mg/l by weight in water at 25°C.
10

Heterocyclic rings according to this invention include cycloaliphatic and cycloaromatic type radicals
15 incorporating an oxygen, sulfur and/or nitrogen atom within the ring system. Representative nitrogen heterocycles include pyridine, morpholine, pyrrole, imidazole, triazole, tetrazole, pyrrolidine, piperidine and piperazine. Suitable oxygen heterocycles include furan, tetrahydrofuran
20 and dioxane. Sulfur heterocycles may include thiophene and tetrahydrothiophene. Among the various heterocycles, it has been found that those incorporating nitrogen are the most active.

25 The term "substituted" is defined in relation to R^1 , R^2 , R^3 as a substituent which is a nitro, halo, cyano, C_1 - C_{20} alkyl, acyl, amino, aminoalkyl, thioalkyl, sulfoxyalkyl, carboxyester, hydroxy, C_1 - C_{20} alkoxy, polyalkoxy and C_1 - C_{40} quaternary di- or trialkylammonium function.
30

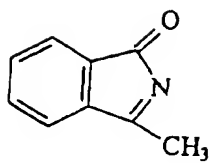
Novel N-acylimine compounds are described below wherein R^1 is hydrogen, R^2 is phenyl with a Z substituent, and R^3 is phenyl with a Y substituent. Very often Z and Y groups are water-solubilizing groups, most commonly being carboxylic
35 acid or salts thereof. Representative structures are as follows:



	Z	Y
IMINE 1	4-CO ₂ H	4-Cl
IMINE 2	4-CO ₂ H	2-Br
IMINE 3	4-Cl	4-CO ₂ H
IMINE 4	H	4-CO ₂ H
IMINE 5	4-CO ₂ H	4-CO ₂ H
IMINE 6	4-CO ₂ H	3-NO ₂
IMINE 7	4-CN	4-CO ₂ H
IMINE 8	4-OMe	4-CO ₂ H
IMINE 9	3-OH	4-Cl
IMINE 10		

Illustrative of cycloaromatic and of heterocyclic N-acylimines are the Imine 11, Imine 12, Imine 13 and Imine 14 compounds whose structures are outlined below.

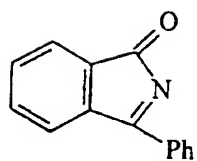
5



IMINE 11

10

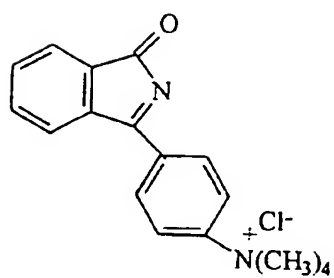
15



IMINE 12

20

25

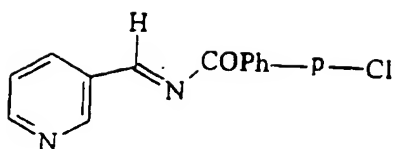


IMINE 13

30

35

5

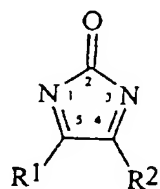


IMINE 14

10

The following further compounds are illustrative of N-acylimines of the present invention.

15



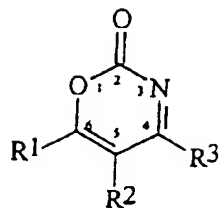
20

25	R ¹	R ²	2H-imidazol-2-ones
	CH ₃	CH ₃	2H-4,5-dimethylimidazol-2-one
	Ph	CH ₃	2H-4-methyl-5-phenylimidazol-2-one
	Ph	Ph	2H-4,5-diphenylimidazol-2-one

30

35

5

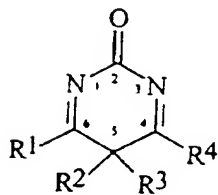


10

R ¹	R ²	R ³	
			2(5H)-oxazalones
CH ₃	CH ₃	CH ₃	4,5,5-trimethyl-2(5H)-oxazalone
CH ₃	CH ₃	Ph	5,5-dimethyl-4-phenyl-2(5H)-oxazalone

15

20

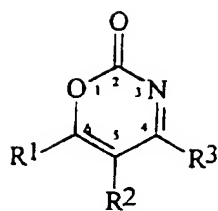


25

R ¹	R ²	R ³	R ⁴	
				5H-2-pyrimidones
CH ₃	CH ₃	CH ₃	CH ₃	5H-4,5,5,6-tetramethyl-2-pyrimidone
Ph	CH ₃	CH ₃	Ph	5H-5,5-dimethyl-4,6-diphenyl-2-pyrimidone

30

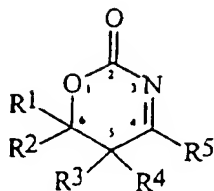
5



10

R ¹	R ²	R ³	
CH ₃	CH ₃	CH ₃	2H-1,3-oxazin-2-ones
CH ₃	CH ₃	CH ₃	4,5,6-tertamethyl-2H-1,3-oxazin-2-one
CH ₃	CH ₃	Ph	5,6-dimethyl-4-phenyl-2H-1,3-oxazin-2-one
Ph	CH ₃	CH ₃	4,5-dimethyl-5-phenyl-2H-1,3-oxazin-2-one

20



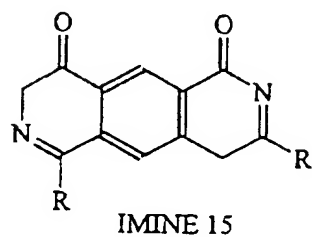
25

R ¹	R ²	R ³	R ⁴	R ⁵	
CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	5,6-dihydro-2H-1,3-oxazin-2-ones
CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	5,6-dihydro-4,5,5,6,6-pentamethyl-2H-1,3-oxazin-2-one
CH ₃	CH ₃	CH ₃	CH ₃	Ph	5,6-dihydro-5,5,6,6-tetramethyl-4-phenyl-2H-1,3-oxazin-2-one

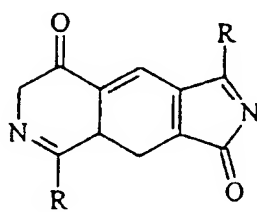
35

5 Multi-heterocyclic ring compounds illustrative of N-acylimines include:

10



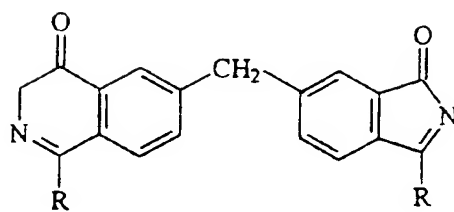
15



20

IMINE 16

25



30

wherein the R groups are independently selected from those defined by
35 R² described above.

The foregoing oxygen transfer agents may be incorporated into detergent bleach compositions along with a further essential component which is a peroxygen compound capable of yielding peroxide anion or peroxyacid in an aqueous solution.

Amounts of oxygen transfer agent suitable for the present invention may range from 0.01 to 10%, preferably from 0.1 to 5%, optimally between 0.5 and 1.5% by weight of the composition.

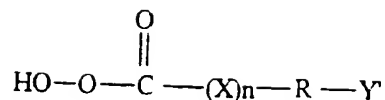
The peroxygen compound may be present from 1% to 65%, preferably from 1.5 to 25%, optimally between about 2 and 10% by weight.

The molar ratio of peroxygen compound to oxygen transfer agent will range from about 250:1 to 1:2, preferably 100:1 to 1:1, optimally between about 25:1 to 2:1.

Peroxyacid and peroxide anion sources are well known in the art. They include the alkali metal peroxides, organic peroxides such as urea peroxide, and inorganic persalts, such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulfates (e.g. Oxone®). Mixtures of two or more such compounds may also be suitable. Particularly preferred are sodium percarbonate, Oxone® and sodium perborate monohydrate.

Alkylhydroperoxides are another suitable class of peroxygen compounds. Examples of these materials include cumene hydroperoxide and t-butyl hydroperoxide.

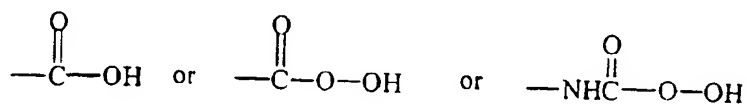
Organic peroxy acids may also be suitable as the peroxygen compound. Such materials have a general formula:



5

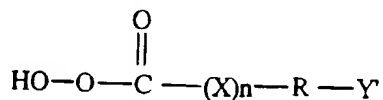
wherein X is oxygen or nitrogen, $n=0$ or 1, R is an alkylene or substituted alkylene group containing from 1 to about 22 carbon atoms or a phenylene or substituted phenylene group, and Y' is hydrogen, halogen, alkyl, aryl or

10



15

When the organic peroxy acid is aromatic, the unsubstituted acid has the general formula:



20

wherein Y' is hydrogen, alkyl, alkylhalogen, halogen, COOH, NHCOOH or COOOH; R is phenylene or arylene; and X is oxygen or nitrogen.

25

Typical monoperoxy acids useful herein include alkyl peroxy acids and aryl peroxy acids such as:

(i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g. peroxy- α -naphthoic acid;

30

(ii) aliphatic, substituted aliphatic and arylalkyl monoperoxy acids, e.g. peroxy lauric acid, peroxy stearic acid, and N,N- phthaloylaminoperoxy caproic acid (PAP).

35

Typical diperoxy acids useful herein include alkyl diperoxy acids and aryldiperoxy acids, such as:

- (iii) 1,12-diperoxydodecanedioic acid;
- 5 (iv) 1,9-diperoxyazelaic acid;
- (v) diperoxybrassylic acid; diperoxysebacic acid and diperoxyisophthalic acid;
- (vi) 2-decyldiperoxybutane-1,4-dioic acid;
- (vii) 4,4'-sulfonylbisperoxybenzoic acid;
- 10 (viii) N,N'-terephthaloyl-di(6-aminoperoxycaproic acid).

Particularly preferred organic acids are N,N-phthaloylaminoperoxycaproic acid, peracetic acid, monoperoxyphthalic acid (magnesium salt hexahydrate), and
15 diperoxydodecanedioic acid. Under certain circumstances, hydrogen peroxide itself may directly be employed as the peroxygen compound.

Optionally, compositions of the present invention may
20 further include a pre-bleach precursor that reacts with peroxide anion or peroxyacid and forms therewith a peracid, percarbonic acid or perimidic acid.

The preferred precursors are N,N,N',N'-tetraacetylene diamine (TAED), tetraacetyl-glycoluril (TAGU), glucose
25 pentaacetate, xylose tetraacetate, sodium acetyloxybenzene sulfonate (SABS) and sodium nonanoyloxybenzene sulfonate (SNOBS). Levels of precursor may range from 0.1 to 40%, preferably from 1 to 10%, optimally from 2 to 8% by weight.

30 Bleach systems of the present invention may be employed for a wide variety of purposes, but are especially useful in the cleaning of laundry. When intended for such purpose, the peroxygen compound and oxygen transfer agent of the
35 present invention will usually also be combined with surface-active materials, detergency builders and other known ingredients of laundry detergent formulations.

The surface-active material may be naturally derived, or synthetic material selected from anionic, nonionic, amphoteric, zwitterionic, cationic actives and mixtures thereof. Many suitable actives are commercially available and are fully described in the literature, for example in "Surface Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch. The total level of the surface-active material may range up to 50% by weight, preferably being from 0.5 to 40% by weight of the composition, most preferably 4 to 25%.

Synthetic anionic surface-actives are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms.

Examples of suitable synthetic anionic detergent compounds are sodium and ammonium alkyl sulphates, especially those obtained by sulphating higher (C_8-C_{18}) alcohols produced for example from tallow or coconut oil; sodium and ammonium alkyl (C_8-C_{20}) benzene sulphonates, sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty acid monoglyceride sulphates and sulphonates; sodium and ammonium salts of sulphuric acid esters of higher (C_8-C_{18}) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralized with sodium hydroxide; sodium and ammonium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C_8-C_{20}) with sodium bisulphite and those derived by reacting paraffins with SO_2 and Cl_2 and then hydrolyzing with a base to produce a random sulphonate; sodium and ammonium C_7-C_{12} dialkyl sulfosuccinates; and olefin sulphonates, which term is used to describe the material

made by reacting olefins, particularly C_{10} - C_{20} alpha-olefins, with SO_3 and then neutralizing and hydrolyzing the reaction product. The preferred anionic detergent compounds are sodium (C_{11} - C_{15}) alkylbenzene sulphonates, sodium (C_{16} - C_{18}) alkyl sulphates and sodium (C_{16} - C_{18}) alkyl ether sulphates.

Examples of suitable nonionic surface-active compounds which may be used, preferably together with the anionic surface-active compounds, include in particular the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C_6 - C_{22}) phenols, generally 5-25 EO, i.e. 5-25 units of ethylene oxide per molecule; the condensation products of aliphatic (C_8 - C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, generally 2-30 EO, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylene diamine.

Other so-called nonionic surface-actives include alkyl polyglucosides, long chain tertiary amine oxides, and fatty amido polyols such as methyl glucamines.

Amphoteric or zwitterionic surface-active compounds such as alkylamidopropyl betaines can also be used in the compositions of the invention. If any amphoteric or zwitterionic detergent compounds are used, it is generally in small amounts in compositions based on the much more commonly used synthetic anionic and nonionic actives.

Soaps may also be incorporated into the compositions of the invention, preferably at a level of less than 30% by weight. They are particularly useful at low levels in binary (soap/anionic) or ternary mixtures together with nonionic or mixed synthetic anionic and nonionic compounds. Soaps which are used are preferably the sodium, or less desirably potassium, salts of saturated or unsaturated C_{10} - C_{24} fatty acids or mixtures thereof.

The amount of such soaps can be varied between 0.5 and 25% by weight, with lower amounts of 0.5 to 5% being generally sufficient for lather control. Amounts of soap between 2 and 20%, especially between 5 and 15, are used to give a beneficial effect on detergency. This is particularly valuable in compositions used in hard water where the soap acts as a supplementary builder.

The detergent compositions of the invention will normally also contain a detergency builder. Builder materials may be selected from (1) calcium sequestrant materials, (2) precipitating materials, (3) calcium ion-exchange materials and (4) mixtures thereof.

- 15 In particular, the compositions of the invention may contain any one of the organic or inorganic builder materials, such as sodium or potassium tripolyphosphate, sodium or potassium pyrophosphate, sodium or potassium orthophosphate, sodium carbonate, the sodium salt of
- 20 nitrilotriacetic acid, sodium citrate, carboxymethylmalonate, carboxymethyloxysuccinate, tartrate mono- and di- succinate, oxydisuccinate, crystalline or amorphous aluminosilicates and mixtures thereof.
- 25 Polycarboxylic homo- and co-polymers may also be included as builders and to function as powder structurants or processing aids. Particularly preferred are polyacrylic acid (available under the trademark Acrysol from the Rohm and Haas Company) and acrylic-maleic acid copolymers
- 30 (available under the trademark Sokalan from the BASF Corporation) and alkali metal or other salts thereof.

These builder materials may be present at a level of, for example, from 1 to 80% by weight, preferably from 10 to 60% by weight.

Upon dispersal in a wash water, the initial amount of peroxygen compound should range anywhere from 0.05 to 250 ppm active oxygen per liter of water, preferably from 1 to 50 ppm. Within the wash media the amount of oxygen transfer agent initially present should be from 0.01 to 300 ppm, preferably from 5 to 100 ppm. Surfactant should be present in the wash water from 0.05 to 1.0 grams per liter, preferably from 0.15 to 0.20 grams per liter. When present, the builder amount will range from 0.1 to 3.0 grams per liter.

Apart from the components already mentioned, the detergent compositions of the invention can contain any of the conventional additives in the amounts in which such materials are normally employed in detergent compositions. Examples of these additives include dye transfer inhibition agents (e.g. polymers based on N-vinylpyrrolidone and N-vinylimidazole), lather boosters such as alkanolamides, particularly the monoethanolamides derived from palmkernel fatty acids and coconut fatty acids, lather-depressants such as alkyl phosphates and silicones, anti-redeposition agents such as sodium carboxymethylcellulose and alkyl or substituted alkylcellulose ethers, stabilizers such as ethylene diamine tetraacetic acid and phosphonic acid derivatives (Dequest®), fabric softening agents, inorganic salts such as sodium sulphate, and, usually present in very small amounts, fluorescent agents, perfumes, enzymes such as proteases, cellulases, lipases and amylases, germicides and colorants.

The oxygen transfer agents in combination with a peroxygen compound may be useful for removing stains both in consumer type products and for industrial applications. Among consumer products incorporating this invention are laundry detergents, laundry bleaches, hard surface cleaners, toilet bowl cleaners, automatic dishwashing compositions and even denture cleaners.

Stained consumer products benefiting from treatment with compositions of this invention may include clothes and other fabrics; household fixtures and applicants such as sinks, toilet bowls and oven ranges; tableware such as drinking glasses, dishes, cookware and utensils; and even dentures. Hair colorants may also be formulated with the bleach composition of this invention. The bleaching system of this invention may also be applied to industrial uses such as for the bleaching of wood pulp.

10

The system of the present invention may be delivered in a variety of product forms including powders, on sheets or other substrates, in pouches, in tablets, in aqueous liquids, or in nonaqueous liquids such as liquid nonionic detergents.

15

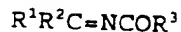
The foregoing description and Examples illustrate selected embodiments of the present invention. In light thereof, various modifications will be suggested to one skilled in the art all of which are within the spirit and purview of this invention.

20

CLAIMS

1. A bleaching composition comprising:

- (i) from 1 to 60% by weight of a peroxygen compound;
- (ii) from 0.01 to 10% of an oxygen transfer agent whose structure is:



wherein:

R^1 may be hydrogen or a C_1 - C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, acyl, heterocyclic ring, alkyl and cycloalkyl radicals;

R^2 may be hydrogen or a C_1 - C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, $R^1C=NCOR^3$, nitro, halo, cyano, alkoxy, keto, carboxylic and carboalkoxy radicals;

R^3 may be a C_1 - C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, nitro, halo and cyano radicals;

R^1 with R^2 and R^2 with R^3 may respectively together independently form a cycloalkyl, heterocyclic, and aromatic ring system; and

- (iii) from 0.5 to 50% of a surfactant.

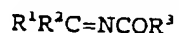
2. A composition according to claim 1 further comprising from about 1 to 80% of a detergent builder.

3. A composition according to claim 1 further comprising an effective amount for cleaning of an enzyme selected from the group consisting of proteases, cellulases, lipases, amylases and mixtures thereof.
4. A composition according to claim 1 delivered in a form selected from the group consisting of a powder, sheet, pouch, tablet, aqueous liquid and nonaqueous liquid.
5. A composition according to claim 1 wherein the peroxygen compound is present in an amount from 1.5 to 25% and the oxygen transfer agent is present in an amount from 0.1 to 5% by weight.
6. A composition according to claim 1 wherein the peroxygen compound is an inorganic material selected from the group consisting of perborate, percarbonate, perphosphate, persilicate and monopersulphate salts.
7. A composition according to claim 1 wherein the peroxygen compound is an organic peroxyacid.
8. A composition according to claim 7 wherein the organic peroxyacid is selected from the group consisting of N,N-phthaloylaminoperoxypropionic acid, peracetic acid, monoperoxyphthalic acid and diperoxydodecanedioic acid.
9. A composition according to claim 1 wherein the peroxygen compound is a bleach precursor.
10. A composition according to claim 1 wherein at least one of R¹, R² and R³ is substituted with a water-solubilizing functional group.
11. A composition according to claim 10 wherein the water-solubilizing functional group is selected from the group consisting of carboxylate, phosphate, phosphonate, sulfate,

sulphonate in acid and salt forms and quaternary ammonium salts.

12. A composition according to claim 1 wherein said substituent on R¹, R² and R³ is a functional unit selected from the group consisting of nitro, halo, cyano, C₁-C₂₀ alkyl, amino, aminoalkyl, thioalkyl, sulfoxyalkyl, carboxyester, hydroxy, C₁-C₂₀ alkoxy, polyalkoxy, C₁-C₄₀ quaternary di- or tri- alkylammonium functional units and mixtures thereof.

13. A method for bleaching a stained substrate, said method comprising contacting said stained substrate in an aqueous medium with a peroxygen compound, a surfactant in an effective amount to clean said substrate and with an oxygen transfer agent whose structure is:



wherein:

R¹ may be a hydrogen or a C₁-C₄₀ substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, acyl, heterocyclic ring, alkyl and cycloalkyl radicals;

R² may be hydrogen or a C₁-C₄₀ substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, R¹C=NCOR³, nitro, halo, cyano, alkoxy, keto, carboxylic and carboalkoxy radicals;

R³ may be a C₁-C₄₀ substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, nitro, halo, and cyano radicals;

R¹ with R² and R² with R³ may respectively together independently form a cycloalkyl, heterocyclic, and aromatic ring system; and said peroxygen compound to oxygen transfer

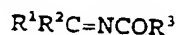
agent being present in a molar ratio ranging from 250:1 to 1:2.

14. A method according to claim 13 wherein the ratio of peroxygen compound to oxygen transfer agent ranges from 100:1 to 1:1.

15. A method according to claim 13 wherein said substrate is selected from the group consisting of fabrics, household fixtures and tableware.

16. A method according to claim 13 wherein said substrate is a denture.

17. A method for bleaching a stained substrate, said method comprising contacting said stained substrate in an aqueous medium with a peroxygen compound and with an oxygen transfer agent whose structure is:



wherein:

R^1 may be a hydrogen or C_1 - C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, acyl, heterocyclic ring, alkyl and cycloalkyl radicals;

R^2 may be hydrogen or a C_1 - C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, $R^1C=NCOR^3$, nitro, halo, cyano, alkoxy, keto, carboxylic and carboalkoxy radicals;

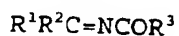
R^3 may be a C_1 - C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, nitro, halo and cyano radicals;

R¹ with R² and R² with R³ may respectively together independently form a cycloalkyl, heterocyclic and aromatic ring system; and

said contacting to achieve bleaching being performed in said medium containing 0.05 to 250 ppm active oxygen from the peroxygen compound, 0.01 to 300 ppm oxygen transfer agent and from 0.05 to 1.0 grams surfactant per liter of medium.

18. A method according to claim 17 wherein the oxygen transfer agent is present from about 5 ppm to about 100 ppm per liter of medium.

19. A bleach whose structure is:



wherein:

R¹ may be hydrogen or a C₁-C₄₀ substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, acyl, heterocyclic ring, alkyl and cycloalkyl radicals;

R² may be hydrogen or a C₁-C₄₀ substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, R¹C=NCOR³, nitro, halo, cyano, alkoxy, keto, carboxylic and carboalkoxy radicals;

R³ may be a C₁-C₄₀ substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, nitro, halo and cyano radicals;

R¹ with R² and R² with R³ may respectively together independently form a cycloalkyl, heterocyclic, and aromatic ring system; and with a proviso that at least one of R¹, R², R³ is substituted with a water-solubilizing functional radical selected from the group consisting of quaternary

ammonium salts, carboxylic acid, phosphoric acid, phosphonic acid, sulfuric acid, sulphonic acid and their salt derivatives.